Glass transition and effective potential in the hypernetted chain approximation

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(November 1997)

We study the glassy transition for simple liquids in the hypernetted chain (HNC) approximation by means of an effective potential recently introduced. Integrating the HNC equations for hard spheres, we find a transition scenario analogous to that of the long range disordered systems with "one step replica symmetry breaking". Our result agree qualitatively with Monte Carlo simulations of three dimensional hard spheres.

The HNC approximation is one of the most widely used approach to describe the density-density correlation function $g(x)$ for liquids at equilibrium [1]. It consists in a self-consistent integral equation that can be derived by a partial resummation of the Meyer expansion, and corresponds to the variational equation for a suitable free-energy functional [2,3]. The simple HNC approach does not by itself allow to detect freezing [4]. The simple inspection of the pair correlation function certainly does not allow to do so, being qualitatively similar in the liquid and in the glass. Freezing, although present, can be hidden if one concentrates on simple equilibrium quantities [5].

In has been recently stressed in [3] that the freezing transition can be detected combining the HNC approximation with the replica method by studying the correlation functions among different replicas of the same system in presence of a potential which couples them. At low temperature (or at high density) one finds a self-consistent solution where different replicas remains correlated also in the limit of zero coupling. This phenomenon correspond to freezing and it goes under the technical name of replica symmetry breaking.

In this letter we pursue this idea of studying the glass transition in the HCN approximation. We are not concerned about the behavior in the glassy phase. Our aim it to use an effective potential recently introduced by two of us [6,7], to study the glass transition of HNC hard spheres in 3D. We compare the results with Monte Carlo simulations of real hard spheres. The conceptual advantage of this approach is that all the subtle points of the usual approach related to replica symmetry breaking are not needed in order to expose the transition.

The effective potential is constructed as follows, for a system described by the coordinates of all the particles $x = (x_1, ..., x_N)$ and with potential energy $H(x) = \sum_{i<j}^{1,N} \phi(x_i - x_j)$.

Let us consider a reference configuration y chosen with probability $\exp(-\beta' H(y))/Z(\beta')$, where $\beta' = 1/T'$ is some arbitrary inverse temperature. Let us define a distance among configuration as $d(x,y) = 1 - q(x,y)$, with the "overlap" $q(x,y)$ defined as $q(x,y) = \frac{1}{N} \sum_{i,j}^{1,N} w(|x_i - y_j|)$. w is an attractive potential that in this letter we choose as $w(r) = \theta(r_0 - r)$. To very different configurations it corresponds large distance and small overlap, to similar configurations small distance and large overlap. We define a constrained Boltzmann-Gibbs measure at temperature T as

$$\mu(x|y) = \frac{1}{Z(\beta, q, y)} e^{-\beta H(x)} \delta(q(x,y) - q) \qquad (1)$$

where $Z(\beta, q, y)$ is the integral over x of the numerator. This conditional measure allows to probe regions of the configuration space having vanishingly small probability, and as we will see, it will help us to reveal the glassy structure hidden in the simple equilibrium approach.

Introducing a Lagrange multiplier conjugated to q to enforce the delta function and integrating over it by saddle point, one see that the free energy associated to (1), $V(q) = -T \log Z(\beta, q, y)$, can be computed as the Legendre transform of $F(\epsilon) = -T \log Z(\beta, \epsilon, y)$ with $Z(\beta, \epsilon, y) = \int dx\ e^{-\beta(H(x) - \epsilon q(x,y))}$. If the coupling ϵ is positive there is an attraction to the reference configuration y. Of special interest will be the cases $\epsilon \to 0^+$, while q will go to a non trivial value. The free-energy $F(\epsilon)$ and the potential $V(q)$ should be self-averaging with respect to the distribution of y, and be therefore just functions of their argument and the temperatures β and β'. From now on, in this letter

we will limit ourselves to the case $\beta = \beta'$ which will be enough to detect freezing in the system. It is conceptually important however to consider the more general case if one would like to describe a system which, after crossing the freezing temperature, remains confined in the vicinity of the configuration where it was last able to thermalize.

In order to compute $F(\epsilon)$ in any physical system we need to average $Z(\beta, \epsilon, y)$ over the distribution of y. This can be done in a convenient way using the replica method, where one writes $\overline{\log Z} = \lim_{r \to 0} \frac{\overline{Z^r} - 1}{r}$, and compute the limit from an analytic continuation from integer r. In principle the replica method can be avoided but it is quite useful to make all the computation quite straightforward. Explicitly:

$$\overline{Z^r} = \int \mathrm{d}x_0 \mathrm{d}x_1 ... \mathrm{d}x_r \ e^{-\beta \sum_{a=0}^{r} H(x_a) + \beta\epsilon \sum_{a=1}^{r} q(x_0, x_a)} \tag{2}$$

we have written $x_0 = y$. The problem is reduced to that of an equilibrium mixture of $r + 1$ species (with $r \to 0$), and is formally similar to the one developed by Given, Stell and collaborators to study liquids in random matrices [8]. The use of the formalism is however different. In [8] the replica method was used to deal with the quenched disorder represented by the medium, while for us the potential is a tool to probe regions of configuration space of small Boltzmann probability and we do not have quenched disorder. The HNC equation can be derived from the following free-energy functional [2,3]

$$- 2\beta F(\epsilon) = \int \mathrm{d}^d x \sum_{a,b=0}^{r} \rho^2 g_{ab}(x) \left[\log g_{ab}(x) - 1 + \beta\phi(x)\delta_{ab}\right] + 2\beta\epsilon \sum_{a=1}^{r} \rho^2 g_{0a}(x) w(x) + \mathrm{Tr} \ \mathbf{L}(\rho h) \tag{3}$$

with $\mathbf{L}(u) = u - u^2/2 - \log(1+u)$, $h_{ab} = g_{ab} - 1$, the trace of $\mathbf{L}$ is intended both on replica indices and in the operator sense in space. The equations, and the relative value of the free energy are obtained extremizing (3) over all the replica correlation functions g_{ab}'s, and extracting the terms of order r.
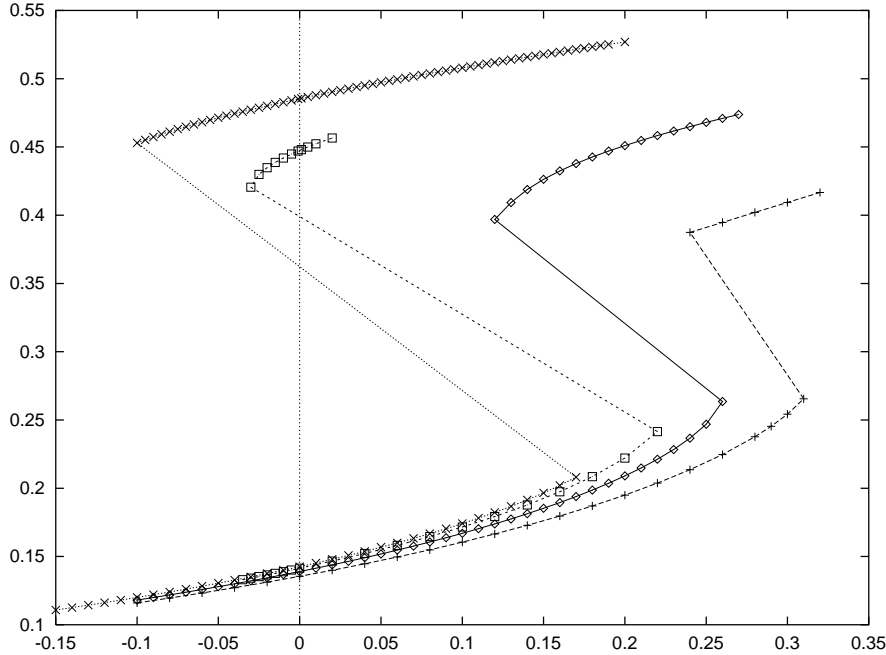

FIG. 1. The behavior of q as a function of ϵ for HNC hard spheres for $\rho = 1.14, 1.17, 1.19, 1.20$. For high enough density q is a multivalued function of ϵ. We have shown only a portion of the curve in the region where it is multivalued. For graphical transparency in this and the next figure we have joined with a line the branches corresponding to the same density.

In order to continue analytically F we use the ansatz $g_{ab} = g_{00}$ for $a = b = 0$, $g_{ab} = g_{10}$ for $a = 0$ or $b = 0$ and $a \neq b$ and $g_{ab} = g_{ab}^*$ for both a and b different from 0. In this paper we will only consider the replica symmetric ansatz $g_{ab}^* = g_{11}\delta_{ab} + g_{12}(1 - \delta_{ab})$. We warn the reader that this ansatz should give the correct value of the potential $V(q)$ for high and low values of q in the liquid phase, replica symmetry breaking effects are to be expected in an intermediate regime [9] even in the liquid phase. The physical meaning of the various elements of g_{ab} within this ansatz is immediate. The element g_{00} represents the pair correlation function of the free system; as such the equation

determining it decouples from the other components in the limit $r \to 0$ and coincides with the usual HNC equation for a single component system. In turn, g_{11} represents the pair correlation function of the coupled system. g_{10} is the pair correlation among the quenched configuration and the annealed one, while g_{12} represents the correlation between two systems coupled with the same quenched system. This last is the analogous of the Edwards-Anderson order parameter in disordered systems [10], and represents the long time limit of the time dependent autocorrelation function at equilibrium [6].
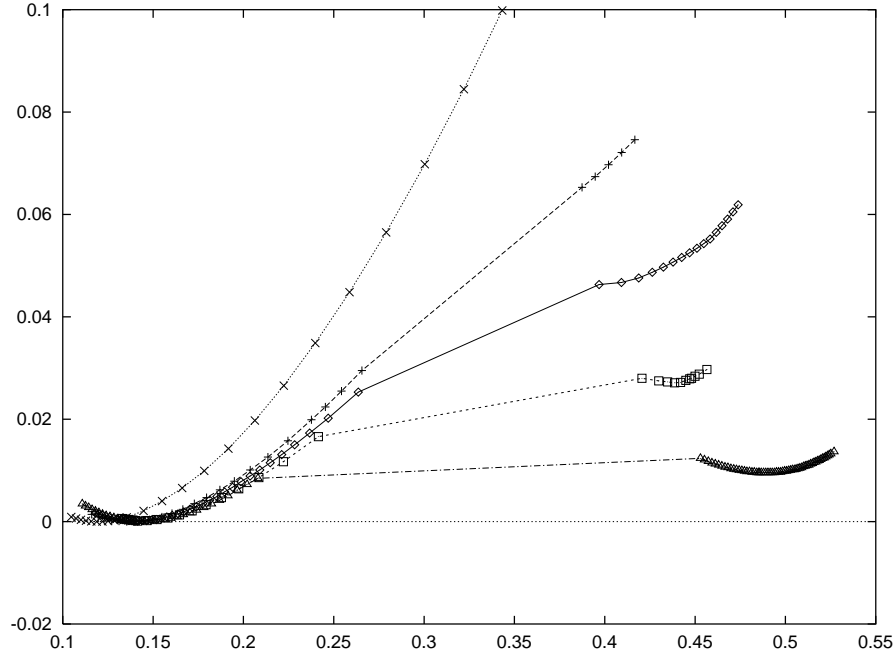

FIG. 2.   The effective potential for HNC hard spheres. From to to bottom $\rho = 1.0, 1.14, 1.17, 1.19, 1.20$. For low density, high up in the liquid phase the potential is convex. In the glass phase two minima are present.

In order to study q as a function of ϵ we have solved the HNC equations in 3D with the hard sphere potential $\phi(r) = \infty$ for $r < 1$, $\phi(r) = 0$ for $r > 1$ for various values of the density (using a space resolution equal to .01 and a large distance cutoff equal to 10). The density ρ is the control parameter of the freezing transition in this problem where there is no temperature. We have rescaled $\beta\epsilon \to \epsilon$, and chosen $r_0 = 0.3$ in the definition of the overlap. We have reconstructed the curves $q(\epsilon)$ and $V(q)$ following the solution of the HNC equations starting from high and low values of ϵ and respectively decreasing or increasing it slowly. We see in figure 1 and 2 that for low enough density q is a single valued function and the potential is convex, with the minimum corresponding to $g_{01}(x) = 1$ for all x. This is a fair description of the liquid phase. Above a critical density $\rho^* \approx 1.14$ the potential loose convexity, and a coupling can induce a transition between a high and a low q phase [7]. For $\rho = \rho_c \approx 1.17$ a second minimum at high q appears, deepening and deepening as the density is increased. The presence of this second minimum shows that above ρ_c the system with is in the glassy phase. If, by means of a large ϵ we prepare the system in the vicinity of y and we then let $\epsilon \to 0$, the system remains confined. It should be noticed that while the shape of $V(q)$ depends on the particular definition of the overlap, the properties of the minima of the potential do not, as they correspond to vanishing coupling.

As it has been discussed in [6,7], the two minima structure is associated to a Gibbs-Di Marzio glass transition scenario. At ρ_c the ergodicity is broken and an extensively large number of metastable states $\mathcal{N} = e^{N\Sigma}$ contributes to the partition function. The relative height of the two minima is exactly equal to the "configurational entropy" Σ, and as we can see in fig. 3, as ρ is increased Σ decreases, until it vanishes at $\rho = \rho_s \approx 1.203$. (The values of ρ_c and ρ_c are compatible with those found in [3], indeed the potential method reproduces the results of replica symmetry braking approach for the static and dynamic critical densities). The shape of the potential is the characteristic one of a system undergoing a first order phase transition. We can use Maxwell construction to locate the transition line in the plane $\epsilon - \rho$, which is shown in fig. 4. The computation as it stands is not consistent for $\rho > \rho_s$: it gives a negative configurational entropy in that region. To describe consistently the behavior there the replica symmetry breaking formalism of [3] is needed.
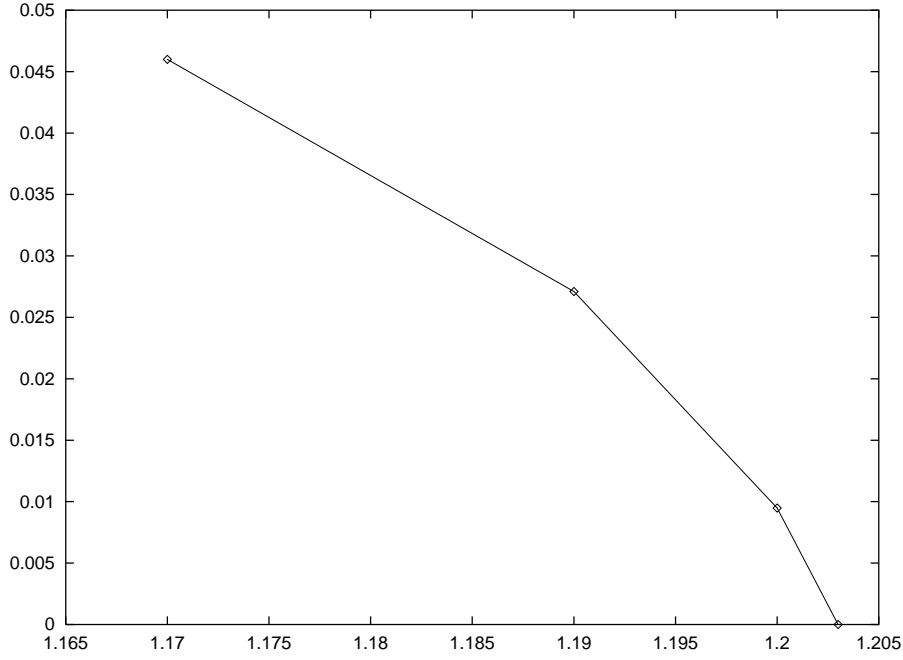
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FIG. 3. The configurational entropy Σ as a function of ρ.

Although we did not try to compare quantitatively the values of the freezing density we get with the one previously found in numerical simulations [11], we have performed our own Monte Carlo simulations to test in a qualitative way the prediction of a first order transition in presence of a coupling with a fixed configuration.
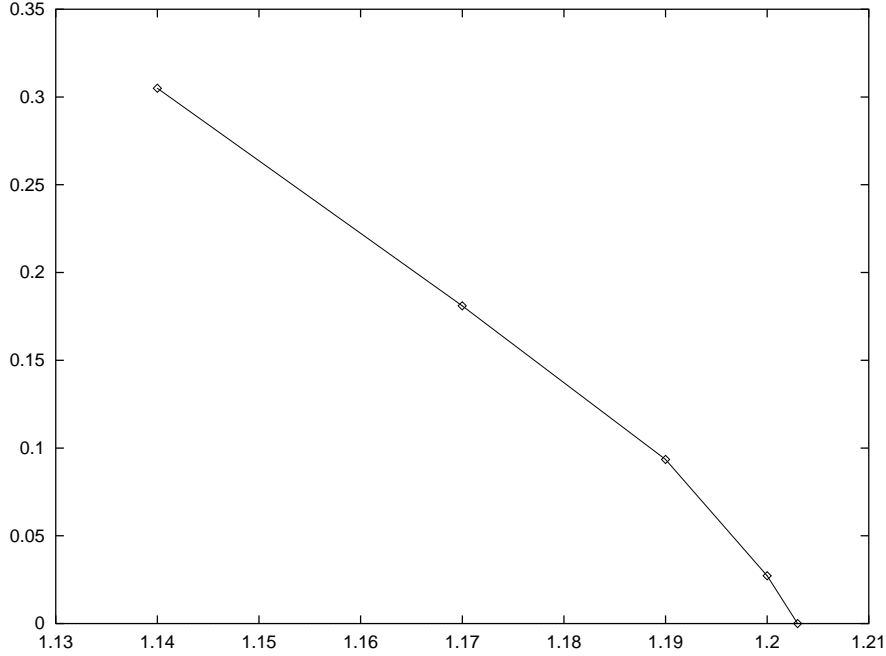

FIG. 4. Phase diagram in the plane $\epsilon - \rho$. A first order transition line terminating in a critical point separates a low q from a high q phase.

To generate configurations at fixed density we start with N particles of zero radius in a three dimensional box with periodic boundary conditions, and we let the radii grow until two particle do get in contact. At that point we make a Monte Carlo sweep and iterate the procedure until the desired density is reached. The volume and the radius (r) are

at the point rescaled in order to have $r = 1$. We thermalize then the system for 4000 Monte Carlo sweeps and use the configuration y reached as "external field" for our coupled replicas experiments. The relatively short thermalization is chosen in order to avoid crystallization. Having generated the configuration y we let evolve a coupled system x. For various densities, we start the evolution from the configuration y with an high value of ϵ and decrease the value of ϵ in units of $\delta\epsilon$, making 2^k Monte Carlo iterations for each value of ϵ. In figure 5 we plot q as a function of ϵ for different values of k. We see that, as it should be expected for a system undergoing a first order phase transition, the curves are smooth for low k and tend to develop a discontinuity for large k. We have presented here results for $\rho = 1.04$. Other simulations(which we do not display here) show lower density the discontinuity occurs at higher ϵ, while it is pushed toward smaller ϵ for higher density. From the quantitative point of view there is about a 20% agreement on the value of the density at which a transition is present in the ϵ-q plane; however the qualitative prediction of a first order transition at vales of ϵ of order 1 is clearly satisfied.
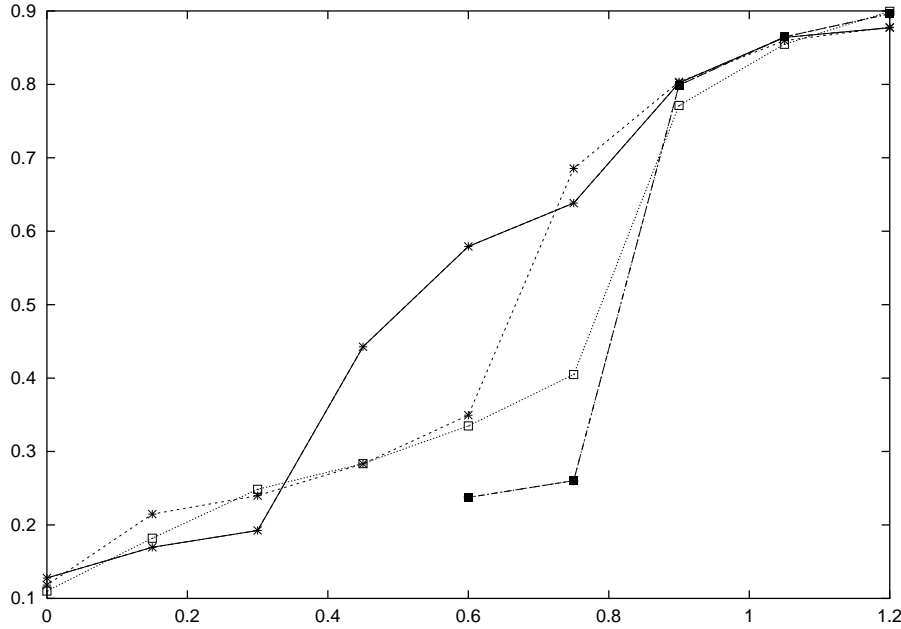

FIG. 5.   The behavior of q as a function of ϵ for a system of 258 particles and $\rho = 1.04$. The different curves correspond different thermalization times 2^k for each value of ϵ. ¿From top to bottom $k = 17, 19, 21, 23$. For larger thermalization times the system seem to develop a first order jump in q.

A different numerical experiment is presented in figure 6. Here we let the system evolve at fixed ϵ starting at time zero from $x = y$ and we plot the overlap as a function of time. Again we observe a behavior compatible with a discontinuity of q as a function of ϵ.
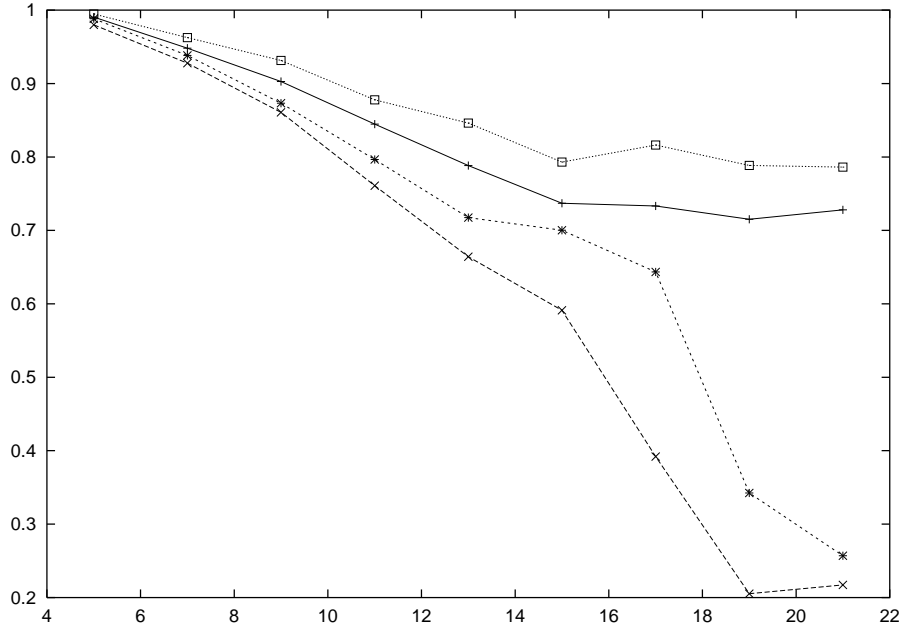
FIG. 6. The overlap as a function of time in a logarithmic scale (the horizontal axis is $\ln_2(t)$ starting from y at time 0 and evolving for fixed ϵ. In this figure $\rho = 1.04$ and from top to bottom $\epsilon = 0.8, 0.7, 0.6, 0.5$, the number of particles is 1024.

We see that the HNC approach predicts a glass transition scenario very close to the one found in systems with "one step replica symmetry breaking" with a non convex [6] effective potential and Gibbs-Di Marzio entropy crisis [12]. The HNC is in this respect a genuine mean-field theory, giving infinite life meta-stable states. In real systems metastable states have finite life time and the potential has to be a convex function of q for any densities. As it has been discussed many times in the application of the theory to real systems [13] the picture should be corrected to take that into account. The density ρ_c, representing the point where the relaxation time diverges in mean-field, becomes a crossover value where the dynamics is dominated by barrier jumping processes [4]. Elucidation of the dynamical processes responsible for restoration of ergodicity beyond mean-field is one of the currently open issue in glass physics.

ACKNOWLEDGMENTS

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